GRAPE WATER: USE AND VALUE OF THE CO-PRODUCT OF CRYOCONCENTRATION OF GRAPE JUICE

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Abstract. Cryoconcentration uses freezing to extract water and concentrate grape juice. The frozen fraction extracted is considered waste. Thus, the use of cryodiluted as an alternative beverage was evaluated. The experiment was conducted in triplicate. The samples were subjected to two stages of cryoconcentration in blocks. The physicochemical analysis of the samples were subjected to analysis of variance and Tukey's test ($p < 0.05$), while the tasted samples were evaluated by analysis of variance and Student's t test ($p < 0.05$). The results demonstrated that total soluble solids, total dry extract, ash, organic matter and total phenolic compounds contents contained in cryodiluted 1 were higher than those found in cryodiluted 2, except for titratable acidity, where both were statistically similar using the Tukey test at the 5.0% significance level. In the tasting analysis, it was possible to identify, using the Tukey test, at a 5.0% level of significance, that the cryodiluted 1 and 2 did not present differences in violet color, clearness, color intensity, acidity, sweetness/acidity balance, astringency, bitterness and taste. The aroma intensity, pleasant and characteristic odor, sweetness and overall evaluation were higher in cryodiluted 1. Grape water proves to be an innovative, natural beverage option with its own chemical composition. The environmental impact of the process of obtaining cryoconcentrated grape juice would be minimized, as the cryodiluted waste generated would be used and sold, reducing the cost of waste treatment.

Keywords: vine water; cryoconcentration; beverage. co-product.

ÁGUA DA UVA: UTILIZAÇÃO E VALORIZAÇÃO DO CO-PRODUTO DA CRIOCONCENTRAÇÃO DO SUCO DE UVA

Resumo. A crioconcentração usa o congelamento para extrair água e concentrar o suco de uva. A fração congelada extraída é considerada resíduo. Assim, avaliou-se o uso do criodiluído como alternativa para bebida. O experimento foi conduzido em triplicata. As amostras foram submetidas a duas etapas de crioconcentração em blocos. As análises físico-químicas das amostras foram submetidas a análise de variância e teste de *Tukey* ($p < 0{,}05$), enquanto que as amostras degustadas foram avaliadas por análise de variância e teste de t *student* ($p < 0{,}05$). Os resultados demonstraram que os teores de sólidos solúveis totais, extrato seco total, cinzas, matéria orgânica e compostos fenólicos totais contidos no criodiluído 1 foram maiores que os encontrados no criodiluído 2, exceto para acidez titulável, onde ambos foram estatisticamente semelhantes pelo teste de Tukey ao nível de 5,0% de significância. Na análise de degustação foi possível identificar pelo teste de *Tukey* ao nível de 5,0% de significância, que o criodiluído 1 e 2 não apresentaram diferenças para cor violácea, limpidez, intensidade de cor, acidez, equilíbrio doçura/acidez, adstringência, amargor e sabor. Já a intensidade de aroma, odor agradável e característico, doçura e avaliação global foram maiores no criodiluído 1. A água da uva revela-se uma opção de bebida inovadora, natural e de composição química própria. O impacto ambiental do processo de obtenção de suco de uva crioconcentrado seria minimizado, já que o resíduo criodiluído gerado seria aproveitado e comerciado, diminuindo o custo com tratamento de resíduos.

Palavras-chave: água da videira; crioconcentração; bebida; co-produto.

1 IINTRODUCTION

Grape juice holds significant importance within the economy of Rio Grande do Sul. The quality of grape juices is primarily influenced by factors such as grape variety, harvest timing, protocols of elaboration and production location (Kaltbach *et al*., 2023). The concentration of grape juice is a significant process for the agroindustry. In 2021, Rio Grande do Sul produced over 160 million liters and sold more than 133 million liters of concentrated juice (Mello; Machado, 2022).

Concentration by freezing is an emerging technique that preserves the nutritional and sensory properties of foods, preserving aromas and levels of thermosensitive compounds (Belén *et al*., 2012; Miyawaki; Inakuma, 2021). With a latent heat of freezing of 335 kJ kg^{-1} of water, cryoconcentration has an energy cost 6.75 times lower than evaporation, with a latent heat of evaporation of 2260 kJ kg-1 of water (Robles *et al*., 2016; Ramaswamy; Marcotte, 2005). However, the degree of concentration achieved is lower than in evaporation processes, but higher than in membrane concentration (Amran *et al*., 2016; Moreno *et al*., 2014; Petzold *et al*., 2016).

The block cryoconcentration technique occurs in three stages: freezing of the liquid, simple gravitational thawing and separation of the concentrated liquid from the ice (Aider; Halleux, 2009; Casas-Forrero; Orellana-Palma; Petzold, 2021; Haas *et al*., 2022). During the freezing of grape juice, the water freezes, releasing the solutes, which accumulate in the solid-liquid interphase, and generates a system of capillaries between the ice crystals occupied by a more concentrated liquid (Petzold; Nirajan; Aguilera, 2013; Vuist; Boom; Schutyser, 2021).

Albergamo *et al*. (2020) conducted a study on a by-product known as 'grape water,' derived from must cryoconcentration. They found significant potential for its utilization, highlighting its resemblance to mineral water in terms of physical-chemical parameters. Moreover, this by-product exhibits nutritional, flavoring, and functional properties inherent to grapes, making it an attractive solution for the agroindustry. Additionally, the authors estimated that approximately 65% of the grape must initially subjected to industrial cryoconcentration is currently directed to sewage treatment plants before entering the public sewage network. That said, the use and valorization of cryodiluted would reduce waste treatment costs, minimize the environmental impact of the cryoconcentration process, and would also generate a potential new wine product for commercialization.

As an intrinsic component of vineyards and comprising the majority of grape water, vegetable water represents a natural resource that warrants utilization and appreciation. The coconut water, evaluated by Pinheiro *et al.* (2005), was found to contain pH levels ranging from 4.95 to 5.01, total soluble solids (TSS) between 5.5–6.0 °Brix, acidity of 0.05–0.07%, sugars ranging from 0.77–3.50%, and minerals such as potassium (104.5–273.1 mg/100 mL), sodium (60.3–108.3 mg/100 mL), and calcium (29.5–34.9 mg/100 mL). The grape water evaluated by Albergamo *et al.* (2020) exhibited similar constituents and properties, but with lower TSS (0.44–0.67 °Brix), implying a potential for a healthier product due to its reduced sugar content. However, Zhang *et al.* (2024) detected biological activities such as DPPH and ABTS in coconut water with values ranging from 66.25% to 87.39% and 37.95% to 83.48%, respectively. Likewise, Albergamo *et al.* (2020) reported analogous findings regarding constituents and properties.

The chemical and nutritional composition presented by cryodiluted motivates the development of techniques that enable its use in the human diet. Furthermore, the technological application of these products would contribute to reducing the environmental impact of the technique. Therefore, this study aimed to evaluate the physicochemical and sensory characteristics of grape water (cryodiluted) for using as an innovative beverage for wine industry.

2 MATERIALS AND METHODS

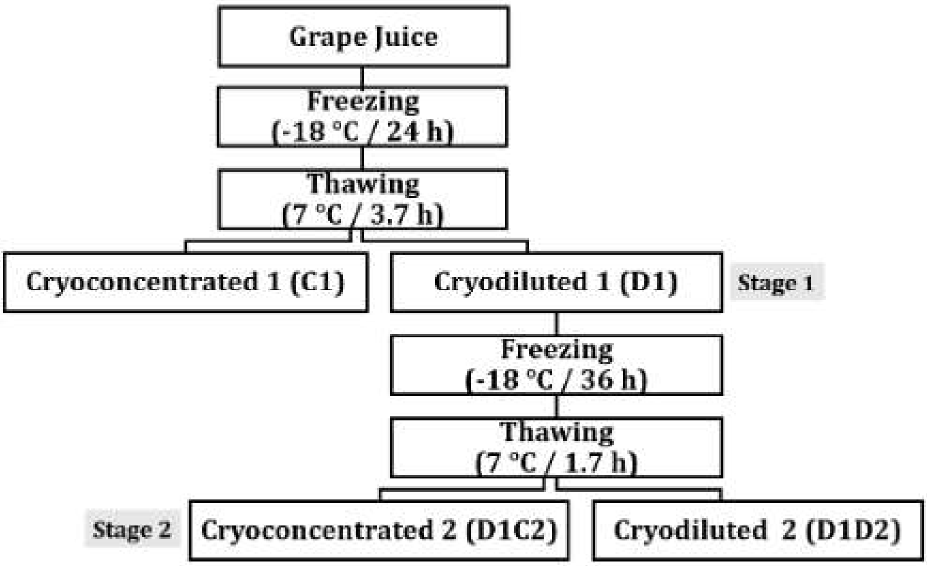
Twenty four bottles of grape juice (0.5 L each) totaling twelve liters (*Vitis labrusca* blend) from the 2021 harvest were made by Embrapa *Uva e Vinh*o, state of Rio Grande do Sul, Brazil.

2.1 Block cryoconcentration protocol

The experiment was conducted in a randomized block design, where the grape juice bottles were divided into three groups of eight bottles (four liters) each. In each group, four liters of grape juice (eight bottles) were packaged in a single five-liter bottle, homogenized, and subjected to two stages of cryoconcentration in blocks. After freezing and thawing, two liters of cryoconcentrated 1 (C1) and two liters of cryodiluted 1 (D1) were obtained. From two liters of D1, one liter of cryoconcentrated 2 (D1C2) and one liter of cryodiluted 2 (D1D2) were prepared, Figure 1.

The second stage of cryoconcentration starting from cryodiluted 1 was carried out with the aim of obtaining cryodiluted 2 with the minimum possible content of total soluble solids (mainly composed of fructose and glucose), allowing future diabetic consumers or those who want a product practically without sugar can consume this beverage.

Figure 1: Block cryoconcentration flowchart.



To obtain the classic oenological parameters and the content of total phenolic compounds, three samples of grape juice, three samples of cryoconcentrated 1, three samples of cryodiluted 1 and three samples of cryodiluted 2 were analyzed in triplicate, coming from samples generated in three two-step cryoconcentration processes.

2.2 Classic oenological parameters

Following the methodology described by the Official Analysis Methods of AOAC INTERNATIONAL (AOAC, 2016), the total dry extract content (AOAC 950.27-1950) was obtained by drying in an oven with air circulation and renewal (Solidsteel SSDi, Piracicaba, Brazil).

According to the methodologies described in the Compendium of International Methods for the Analysis of Wines and Musts of the International Organization of Vine and Wine (OIV, 2022), the relative density (OIV-MA-AS2-01) and the total soluble solids content (OIV-MA-AS2-01A/2021) were determined using a concentration densimeter (Anton Paar DMA 4500M, Austria), the ash (OIV-MA-AS2-04) by incineration in a muffle furnace (Electra M10, Germany), the pH (OIV-MA-AS313-15) with Hanna Instruments pH meter (HI 3221, Romania), titratable acidity (OIV-MA-AS313-01) by titration with 0.1 N NaOH. The organic matter content was obtained by subtracting the total soluble solids content from the ash content.

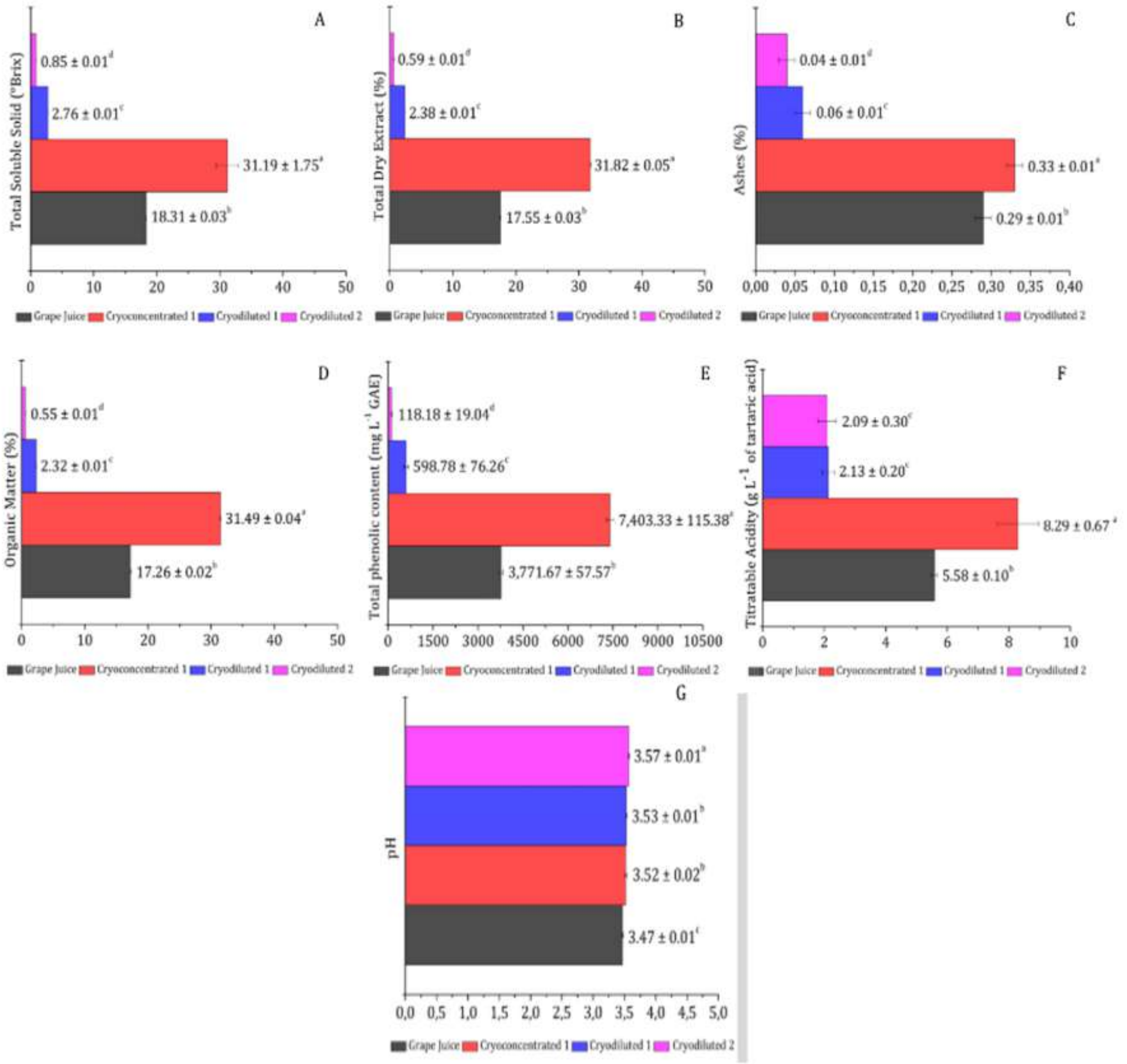
2.3 Total phenolic compounds content

Content of total phenolic compounds was determined at 765 nm, after reaction with Folin-ciocalteu reagent, using a UV-VIS spectrophotometer (Shimadzu 1800, Kyoto, Japan), according to the colorimetric method used by Lazzarotto *et al*. (2020). Gallic acid was used as standard and the levels of total phenolic compounds were expressed in mg of gallic acid equivalents (GAE) per liter of sample (mg L-1 GAE).

2.4 Tasting

According to the methodology developed by Pereira *et al.* (2023), the tasting of samples D1 and D1D2 were carried out at Embrapa *Uva e Vinho*, in Bento Gonçalves-RS, Brazil, conducted in individual cabins under white light. Samples D1 and D1D2 were served in a volume of 50 mL, in ISO Type tasting glasses, as recommended by ISO 3591:1977 (ISO, 1977), at a temperature of $7.0 \pm 2.0\,^{\circ}$C (refrigerator cooling temperature). Each sample

Figure 2: Effects of cryoconcentration on the prospection of total soluble solids (A), total dry extract contents (B), ashes (C), matter organic (D), total phenolic content (E), titratable acidity (F), and pH (G) of grape juice, cryoconcentrated and cryodiluteds.



Distinct letters on the graphic shows significant statistic differences in the samples (Tukey's test at 5%).

was coded with three digits. A sensory panel composed by nine professional enologists from Embrapa Uva e Vinho, with experience in sensory analysis of grape-based beverages, analyzed samples in order to discriminate their sensory perceptions in terms of visual (violet color, clarity and color intensity), olfactory (aroma intensity, pleasant and characteristic odor, and unpleasant odor) and gustatory (sweetness, acidity, sweetness/acidity balance, astringency, bitterness, and unpleasant taste) attributes, and overall assessment.

2.5 Statistical analysis

All analyzes were performed in triplicate and data were submitted to analysis of variance, Tukey's test at $p < 0.05$ and student t test ($p < 0.05$) using IBM SPSS Statistics version 20.0 (Boston, MA, USA).

3 RESULTS AND DISCUSSIONS

3.1 Classic oenological parameters

The cryoconcentration process aims to generate cryoconcentrated grape juice with increased concentrations of sugars, flavors, and other soluble compounds, and the cryodiluted being a co-product of the process. Total soluble solids (TSS) contents increased from 18.31 °Brix (initial juice) to 31.19 °Brix (C1) in the first block cryoconcentration stage. Nevertheless, TSS decreased to 2.76 °Brix in D1. In the second cryoconcentration stage, the TSS decreased to 0.85 °Brix (D1D2), Figure 2A. With greater efficiency, using an industrial cryoconcentrator, Albergamo *et al.* (2020) reduced the total soluble solids content in Grillo and Moscato D'Alessandria musts from 23.28 °Brix and 21.06 °Brix to 0.67 °Brix and 0.44 °Brix, respectively.

In the first cryoconcentration stage, the total dry extract (TDE) content increased from 17.55% in the initial juice to 31.82% in C1, leaving 2.38% in D1. In the subsequent cryoconcentration step, D1D2 contained 0.59% TDE, Figure 2B. Starting from an ashes content of 0.29% (initial juice), 0.33% in C1 and 0.06% in D1 were obtained. D1D2 had an ashes content of 0.04%, Figure 2C. Matter organic contents (MOC) increased from 17.26% (initial juice) to 31.49% (C1) in the first cryoconcentration stage. MOC decreased to 2.32% in D1. In the second cryoconcentration stage, the MOC decreased to 0.55% in D1D2, Figure 2D.

As shown in Figure 2E, the first cryoconcentration stage doubled the total phenolics content (TPC) in C1, retaining 598.78 $mg\,L^{-1}$ GAE in the frozen fraction (D1). In the second cryoconcentration stage, 118.18 $mg\,L^{-1}$ GAE were retained in D1D2. Albergamo *et al.* (2020) detected a TPC of 28.60 $mg\,L^{-1}$ GAE and 34.70 $mg\,L^{-1}$ GAE in the cryodiluted of *Grillo and Moscato D'Alessandria* varieties, respectively. The high content of phenolic compounds in these studies may be related to the grape variety, local ripening conditions, and the elaboration process.

Organic acids from the grape juice (5.58 $g\,L^{-1}$ of tartaric acid) partially migrated to cryoconcentrated 1 (8.29 $g\,L^{-1}$ of tartaric acid), 2.13 $g\,L^{-1}$ of tartaric acid being retained in D1, Figure 2F. The second cryoconcentration stage retained in the frozen fraction (D1D2) 2.09 $g\,L^{-1}$ of tartaric acid. With greater separation of organic acids, Albergamo *et al.* (2020) went from titratable acidity levels of 7.17 $g\,L^{-1}$ and 5.68 $g\,L^{-1}$ of tartaric acid in the must to 1.32 $g\,L^{-1}$ and 1.26 $g\,L^{-1}$ of tartaric acid in the cryodiluted from the *Grillo and Moscato D'Alessandria* varieties, respectively.

The first cryoconcentration step increased the pH levels in C1 (3.52) and D1 (3.53). D1D2 contains the highest pH among the samples at 3.57, Figure 2G. With higher magnification, Albergamo *et al.* (2020) went from pH 3.72 in must to 4.64 in cryodiluted (*Grillo*) and pH 2.86 in must to 3.39 in cryodiluted (*Moscato D'Alessandria*). The results obtained in both studies demonstrated the influence of the reduction in organic acid content and the presence of alkali and alkaline earth metal salts on the pH parameter of cryodiluted samples (Miele; Fioravanço, 2013).

The efficiency of the cryoconcentration process can be measured by the degree of purity of the cryodiluted (Pazmiño *et al.*, 2017). D1 has more solids than D1D2 since the original sample has higher solids content. The migration of solutes to the frozen phase is directly influenced by the initial amount of solutes. In stages subsequent to the first cryoconcentration stage, Boaventura *et al.* (2013) and Aider and Halleux (2008) obtained cryodiluteds with higher solute content. Cryodiluteds are healthy food alternatives made up of water, minerals, sugars and bioactive compounds produced naturally in the vineyard. Considered a residue from the cryoconcentration process, cryodiluted represented a sustainable, viable, innovative and profitable solution for the wine agroindustry. This co-product represents around 75% (v/v) of the initial grape juice.

3.2 Tasting

The results of samples D1 and D1D2 showed no differences using the Student t test, at a 5.0% level of significance for the attributes violet color, clearness and color intensity (Figure 3). The visual sensory descriptors presented for D1 were slightly intense milky violet color, cloudy and opaque appearance, clearer, good color, veiled and bright. For D1D2, they had a more intense milky violet color, a cloudy and opaque appearance, less clear, a good, veiled, duller color.

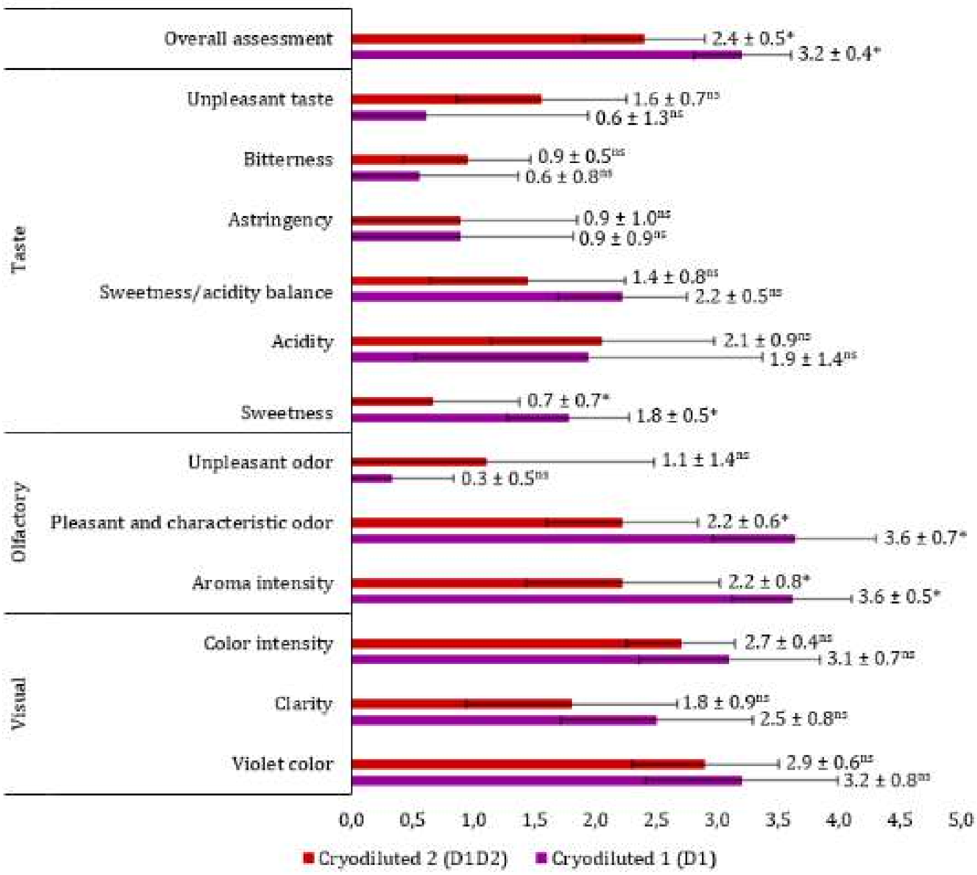
The results of samples D1 and D1D2 did not show a difference using the Student t test ($p < 0.05$) for the unpleasant odor attribute. However, they showed a difference using the Student t test, at a 5.0% level of significance for the attributes aroma intensity and pleasant and characteristic odor, with sample D1 being superior to D1D2 for all evaluators. The olfactory sensory descriptors presented for D1 were fruity, foxy aroma and good typicality of

Vitis labrusca. For D1D2, they had a discreet fruity aroma, almost neutral, without foxed characteristics, without aroma. The tasting demonstrated that the second stage of cryoconcentration provided a higher retention of aromatic compounds in cryoconcentrated 2, as the evaluators had a greater perception of aromas in the D1.

D1 and D1D2 showed no differences using the Student t test, at a 5.0% level of significance for the attributes acidity, sweetness/acidity balance, astringency, bitterness and unpleasant taste. However, they showed a difference using the Student t test ($p < 0.05$) for the sweetness attribute, with sample D1 being superior to D1D2 for all evaluators. The analysis of total soluble solids consolidates this result, since sample D1 is 3.25 times higher than D1D2. Thus, as the titratable acidity levels did not make a significant difference between D1 and D1D2, in the perception of those evaluated and in the laboratory analysis.

The taste sensory descriptors presented for D1: neutral flavor, less watery, medium acidity, low sweetness, but balanced. For D1D2: neutral flavor, watery, low sweetness, cooked fruit; watery, without structure and flavor, dry, less grape flavor and medium acidity.

Figure 3: Sensory analysis of grape water samples.



The lines represent the average of the attribute scores and the error bars represent the standard deviations. The symbol (*) indicates difference and (ns) indicates that there is no difference between the cryodiluteds ones by the Student t test ($p < 0.05$).

D1 and D1D2 showed a difference using the Student t test, at a 5.0% level of significance for the overall assessment attribute, with sample D1 superior to D1D2 for all evaluators. Sensory descriptions demonstrated that sample D1 was superior to D1D2. The chemical composition associated with the sensory characterization of D1 and D1D2 made it possible to raise the possibility of using them as beverage.

4 CONCLUSION

With three times the TSS and five times the TPC of D1D2, the beverage D1 expressed a greater perception of sweetness and intensity of aromas, being sensorially better evaluated than D1D2. The findings highlight the potential of grape water as an alternative beverage, characterized by its chemical composition, and by being completely natural as it comes directly from grapes. Grape water appears as an innovative solution, offering benefits such as reducing the environmental impact of cryoconcentration and reducing waste treatment costs from this technology.

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